Calcium weathering in forested soils and the effect of different tree species

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Abstract. Soil weathering can be an important mechanism to neutralize acidity in forest soils. Tree species may differ in their effect on or response to soil weathering. We used soil mineral data and the natural strontium isotope ratio $^{87}Sr/^{86}Sr$ as a tracer to identify the effect of tree species on the Ca weathering rate. The tree species studied were sugar maple (*Acer saccharum*), hemlock (*Tsuga Canadensis*), American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), white ash (*Fraxinus Americana*) and red oak (*Quercus rubra*) growing in a forest in northwestern Connecticut, USA. Three replicated sites dominated by one of the six tree species were selected. At sugar maple and hemlock sites the dominant mineral concentrations were determined at three soil depths. At each site soil, soil water and stem wood of the dominant tree species were sampled and analyzed for the $^{87}Sr/^{86}Sr$ ratio, total Sr and Ca content. Atmospheric deposition was collected and analyzed for the same constituents. Optical analysis showed that biotite and plagioclase concentrations were lower in the soil beneath hemlock than beneath sugar maple and suggested species effects on mineral weathering in the upper 10 cm of the mineral soil. These results could not be confirmed with data obtained by the Sr isotope study. Within the sensitivity of the Sr isotope method, we could not detect tree species effects on Ca weathering and calculated Ca weathering rates were low at all sites ($< 60 \, mg \, m^{-2} \, yr^{-1}$). We found a positive correlation between Ca weathering and the total Ca concentration in the surface soil. These results indicate that the absolute differences in Ca weathering rate between tree species in these acidic surface soils are small and are more controlled by the soil parent material (plagioclase content) than by tree species.

Introduction

There is substantial evidence that acid rain has depleted exchangeable Ca pools in many soils of forests of the northeastern United States during the last century (e.g. Lawrence et al. (1995) and Likens et al. (1996, 1998)), and consequently has decreased the capacity of soils to neutralize acidity. However, numerous studies showed some biologic control over the status of the exchangeable Ca pool and pH in surface soils (Alban 1982; Bockheim 1997; Boettcher and Kalisz 1990; Johnson and Todd 1990; Klemmedson 1987; Nordén 1994). Except for replicated experiments where trees were planted (Binkley and Valentine 1991; Chalinor 1968; Eriksson and Rosen 1994), it is not easy to determine whether trees cause changes in

soil exchangeable Ca and pH, or whether these soil properties reflect differences in parent material, which in turn influences tree distribution. Van Breemen et al. (1997) and Finzi et al. (1998) tried to separate effects of tree species from effects of parent material, by measuring soil parent material properties (soil texture and elemental composition) and soil properties easily affected by trees (exchangeable Ca and pH). These studies, at Great Mountain Forest, northwestern Connecticut, concluded that the soils' parent material and its effect on tree distribution must be considered in determining tree species effects on exchangeable Ca and soil pH.

Trees may directly affect the exchangeable Ca pool in surface soils through their influence on chemical weathering. Several authors have reported apparent differences in mineral weathering caused by different tree species (Augusto et al. 2000; Bergkvist and Folkeson 1995; Bouabid et al. 1995; Quideau et al. 1996; Spyridakis et al. 1967; Tice et al. 1996). Species-induced weathering has been related to the production of organic acids in the soil and the ability of these acids to complex metals or affect soil pH (Antweiler and Drever 1983; Kodama et al. 1983; Lundström and Öhman 1990; Raulund-Rasmussen et al. 1998; Tan 1980; Van Hees and Lundström 1998). Other workers have argued that exudates by roots or ectomycorrhizal fungi promote mineral weathering in the rhizosphere (Gobran et al. 1998; Ochs et al. 1993; Van Breemen et al. 2000). Trees may also increase soil weathering rates by modifying the soil pH through CO_2 production (Cawley et al. 1969), by net cation uptake from the soil, or by enhancing deposition of atmospheric acids (Bergkvist and Folkeson 1995; Fölster 1985). We predict that tree species grown on soils poor in base cations and that are able to lower soil pH through mechanisms mentioned above and/or are associated with ectomycorrhizal fungi, have a larger impact on the Ca weathering rate in the soil than tree species that do not have these characteristics.

Many studies concerning biologic control of mineral weathering have been done under laboratory conditions or with manipulated field experiments. Determining weathering rates in the field remains difficult (e.g. Likens et al. (1998)). Recently the strontium isotope ratios, $^{87}Sr/^{86}Sr$, have been used as a tracer to separate the Sr input derived from soil weathering and the Sr coming from the atmosphere. The similar geochemical behavior of Ca and Sr (Graustein 1989) has led to the use of Sr isotopes to estimate Ca weathering rates in natural terrestrial ecosystems (Åberg et al. 1989; Bailey et al. 1996; Clow et al. 1997; Miller et al. 1993; Wickman and Jacks (1992, 1993)). This method i) provides estimates of *in situ* Sr and Ca weathering rates; ii) is not affected by weathering from deeper unconsolidated material; iii) requires no site specific Sr or Ca mass balance calculations. However, in soils with high mineralogical heterogeneity where minerals have distinct $^{87}Sr/^{86}Sr$ ratios and Sr weathering rates, this method becomes more difficult to apply successfully.

The objective of this research was to identify the effect of different tree species on the chemical weathering rate of Ca in the soil and to quantify Ca weathering rates at sites differing in tree species composition and soil parent material using Sr isotopic and soil mineral data.

Methods

Study site

This research was done in a watershed near Camp Pond in Great Mountain Forest (GMF), northwestern Connecticut, USA (see Canham et al. (1994) and Pacala et al. (1994)). During the last ice age a thin mantle of compacted clayey sandy micaceous till covered more than 90% of the mica schist bedrock surface of the area. Following deglaciation, large masses of stagnant ice occupied current swamp areas (Colton 1968). The soils formed on the glacial till at Camp Pond are acidic, well-drained, sandy loams classified as Typic Dystrochrepts (Hill et al. 1980) with depths ranging between 50–70 cm. X-ray diffraction showed that significant amounts of plagioclase, alkali-feldspars and mica (biotite) are present in the soil (F.A. Dijkstra, unpublished). The uneven surface is scattered with numerous glacially transported boulders. A mixture of hardwood and coniferous trees covers the soils. We considered three endomycorrhizal trees (sugar maple -*Acer saccharum*-, red maple -*Acer rubrum*, L.-, and white ash -*Fraxinus Americana*) and three ectomycorrhizal trees (eastern hemlock -*Tsuga Canadensis*, Carr.-, American beech -*Fagus grandifolia*, Ehrh.-, and northern red oak -*Quercus rubra*, L.). For each tree species three sites were selected where each site was dominated by one of these six species (Figure 1). Four to ten mature trees of one of the six tree species dominated each site in an area with a diameter of approximately 25 m. The study site at Camp Pond is in a second growth ($\sim$80–130 yr. old) stand with a history of logging but not of agriculture.

Sampling

Atmospheric deposition was collected in two collectors at a clearing close to Camp Pond (see Figure 1). Collectors, 1 m above the ground, were made of a polyethylene funnel (diam. 20 cm), connected to a neoprene tube draining into a partially buried polyethylene bottle. A plug of polyester fiber in the funnel prevented particulate debris entering the bottle. Atmospheric deposition was collected weekly from May until October in 1997, 1998, and 1999 and stored in the dark at 4 °C prior to analysis.

At each site three soil cores (diam. 4.5 cm) were taken at depths of 0 to 20 cm and 50 to 70 cm in the spring and summer of 1997, and at depths of 0 to 10 cm and 20 to 30 cm in the summer of 2000. Soil samples were bulked for each depth and for each site, then dried for 48 hours at 105 °C and sieved (mesh size 2 mm). For soil micromorphological observations thin sections were prepared according to Fitz-Patrick (1970), from soil samples taken at 0 to 10, 20 to 30, and 50 to 70 cm depth beneath sugar maple and hemlock sites.

Tension lysimeters (Rhizon SMS, Eijkelkamp) were installed at each tree sampling site at a depth of 20 cm in the summer of 1997. The lysimeters were above groundwater level during the whole year. The lysimeters were produced from a hydrophilic porous polymer connected to PVC tubing. Soil solutions were obtained
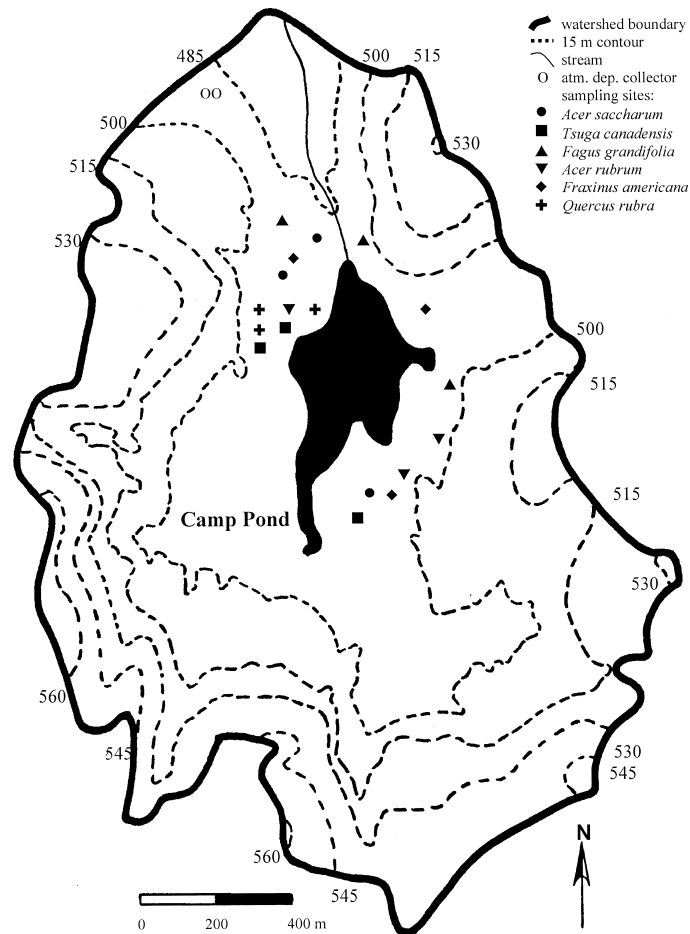
Figure 1. Camp Pond watershed and the site locations at Great Mountain Forest.

by connecting evacuated bottles (40 kPa) to the lysimeters. Soil solution samples were collected during the spring of 1998. All materials for solution sampling were cleaned in 50% hydrochloric acid and rinsed with nanopure water before use. Blanks were determined in 200 ml of nanopure water rinsed through the lysimeters and the atmospheric deposition collectors. Strontium contamination from the lysimeter contributed < 0.04% of the Sr in the soil solution concentration, and the atmospheric deposition collectors released < 0.2% of the Sr found in atmospheric deposition.

Wood samples (three cores, diam. 0.5 cm, to the center of the stem at breast height of the dominant tree) were taken from one tree at each site. At one site with an area of approximately 15 × 15 m, six individual beech trees, between 40 and 130 years old, were sampled separately. Wood cores were dried for four days at 70 °C.

Chemical and mineralogical analyses

Weekly atmospheric deposition and soil solution were analyzed for Ca with a Perkin-Elmer Inductively Coupled Plasma Emission Spectrometer (ICP). To obtain enough Sr from the atmospheric deposition for analyses, weekly samples were bulked, so that four samples were obtained over the sampling period in 1998. Atmospheric deposition and soil solution sub samples were measured for Ca content with the ICP. To analyze the Sr content and the $^{87}Sr/^{86}Sr$ ratio, atmospheric deposition and soil solution samples were spiked with ^{84}Sr and afterwards evaporated. To minimize blank contributions all reagents were distilled in Teflon and sample processing was done in acid-cleaned Teflon. Samples were dissolved in concentrated HNO_3 and evaporated. Samples then were dissolved in 3 *N* HNO_3 and transferred into centrifuge tubes and centrifuged for 4 minutes at 9000 rpm. Strontium was separated by ion exchange chromatography in pre-cleaned quartz columns containing Sr-Resin (ElChroM Industries Inc.). All metals, except Sr, were stripped from the column with 20 column volumes of 3 *N* HNO_3 and afterwards Sr was collected with 10 column volumes of H_2O. Samples were evaporated and nitrated twice with concentrated HNO_3 to reduce organic material.

The organic matter content of soils from 0 to 10, 20 to 30, and 50 to 70 cm depth was measured by loss on ignition. Approximately 10 g of oven-dried soil was combusted in a muffle oven at 450 °C for 8 hours. The soil texture of these same samples was analyzed on a Coulter LS230 laser grain-sizer with a 5 mW, 750 nm laser beam (after Buurman et al. (1997)). Soil samples from 0 to 20 cm depth were analyzed for total Sr and Ca with X-ray fluorescence (XRF). Ground samples (0.6 g) were melted with 2.4 g of $Li_2Br_4O_7$ at 1100 °C for four hours. The resulting glass beads were analyzed using a Philips PW 1404 XRF Spectrometer, using standard reference samples prepared similarly (after Buurman et al. (1996)).

Mineral surface areas, rather than mineral concentrations, need to be considered in predicting soil weathering rates (White et al. 1996). We measured surface areas of minerals in soil samples taken from 0 to 10, 20 to 30, and 50 to 70 cm depth at sugar maple and hemlock sites. We expected that samples taken at these depths would give a good representation of the distribution of minerals in the soil profile, and that these two tree species would be most divergent in their effect on soil weathering. Using these data we were able to do a sensitivity analysis on the Ca weathering rates that we calculated (see below). To estimate surface areas of individual weatherable minerals, we considered the grain size fractions of 10–50 (separated by sedimentation, using Stokes Law) and of 50–500 μm (separated by sieving), after removing soil organic matter by adding 10% H_2O_2 at 80 °C until dissapearance of dark staining by humus, followed by ultrasonic treatment. Subsamples of the fractions were impregnated and cut and polished into 30 μm × 1 cm × 1 cm sized thin sections. The uncovered thin sections from the 50 to 500 μm fraction were stained with K_3CoNO_2 and hemateine to detect plagioclase and alkali-feldspars respectively according to Van der Plas (1966). A digital petrographic microscope (COOLSNAP, Roper Scientific Inc.) was used to measure two-dimensional surface areas of all minerals, and of biotite, plagioclase, and alkali-feldspar sepa-

rately, with digital image analysis software (Image-Pro Plus, Media Cybernetics). The grain size distributions were almost identical in all samples, hence the relationship between two-dimensional surface areas and actual three-dimensional mineral surface areas is the same for each sample.

Minerals of the 50 to 500 μm fraction of the soil samples from 50 to 70 cm depth were separated using heavy liquids and magnets prior to hand picking under a binocular microscope. The 10 to 50 mg mineral separates were better than 99% pure. The predominant soil minerals were separated (quartz, plagioclase, alkali-feldspar, biotite, muscovite, and vermiculite). Sub samples of the bulk soil (from 50 to 70 cm depth) and stem wood were ground with a KLECO Pulverizer (model 4200). Ground soil samples and stem wood samples were ashed at 600 °C in platinum crucibles. Bulk and mineral samples were treated with 40% HF and concentrated HNO_3, evaporated and dissolved in 6 N HCl in Teflon beakers. An aliquot of the samples was taken and diluted ten times for measurement of Sr and Ca concentrations by ICP. Another aliquot was evaporated and dissolved in 3 N HNO_3 and Sr was separated in the same way as for the atmospheric deposition and soil solution samples.

Total Sr and the $^{87}Sr/^{86}Sr$ ratio were measured by thermal ionization mass spectrometry (Finigan Mat 261 and 262 RPQ-Plus). All samples were loaded on annealed rhenium filaments. Dynamic triple jump measurements were performed on the non-spiked samples (soil and stem wood samples) while the spiked samples (solution samples) were measured in static mode providing both total Sr and the $^{87}Sr/^{86}Sr$ ratio. Mass fractionation during the measurements were corrected by normalizing to the $^{86}Sr/^{88}Sr$ ratio, set at 0.1194. Each mass spectrometer run consisted of at least 50 individual measurements and the standard error of the final $^{87}Sr/^{86}Sr$ ratio was smaller than 0.00002. The $^{87}Sr/^{86}Sr$ ratio measured in the spiked samples was corrected for the amount of spike added. The international standard NBS 987 was measured periodically. Typical values for the dynamic and static runs were 0.710243 ± 0.000012 (n > 50) and 0.710231 ± 0.000018 (n = 24) respectively. Total Sr blanks for the chemical separation procedure were < 200 pg or generally < 0.02% of the Sr loaded for each sample.

Calculations and statistical analyses

The proportion of Sr measured in the stem wood derived from weathering $X_{B,W}$ can be calculated with a linear mixing equation using the two sources of Sr in the tree-soil system, soil weathering and atmospheric deposition, as the end members (Graustein and Armstrong 1983; Graustein 1989):

$$X_{B,W} = \frac{Sr_B - Sr_D}{Sr_W - Sr_D} \tag{1}$$

where Sr_W is the Sr isotope ratio $^{87}Sr/[^{87}Sr + {}^{86}Sr]$ of the weathering end member, Sr_B is the isotope ratio measured in the stem wood and Sr_D is the isotope ratio of

the atmospheric end member. This equation assumes that there is a single weathering end member in the rooting zone of the soil. Because concentrations of weatherable minerals, each with different Sr isotope ratios and weathering rates, vary with soil depth at our site, no single weathering end member can be identified in these soils. This problem can be dealt with in different ways. Some studies have tried to simulate soil weathering under laboratory conditions. By leaching rock or soil with an inorganic or organic acid the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio for the weathering end member was obtained from the leachates (Miller et al. 1993; Wickman and Jacks (1992, 1993); Wickman 1996). Organic extractions however, are easily contaminated with Sr. Moreover, leaching with strong inorganic acids is a poor substitute for natural weathering, and in fact is not much different than completely dissolving soil minerals. Earlier studies did not tackle the problem of variable soil mineralogy with depth. Bailey et al. (1996) based the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio of the weathering end member on the abundance and distribution of different minerals at various depths, and calculated an isotope ratio for the weathering end member that happened to be close to the Sr isotope ratio of the bulk soil.

We used the Sr isotope ratio of the organic-poor, but mineral-rich soil at 50 to 70 cm depth for the weathering end member to minimize contamination from exchangeable Sr with a partly atmospheric Sr signature. We considered uncertainties about the nature of the composition of the weathering end member (resulting from variable soil mineralogy with depth), and uncertainties about the relative weathering rates of the dominant weatherable minerals. We varied the plagioclase:biotite surface area ratios and ratio of Sr weathering rates from plagioclase and from biotite within conceivable limits to obtain different possible weathering end members for each of the sugar maple and hemlock sites. With this sensitivity analysis we incorporated the notion that biotite usually weathers faster than plagioclase (Blum et al. 1994; Blum and Erel 1997). First we kept the ratio of plagioclase:biotite Sr weathering rates at 1:3 and varied the overall plagioclase:biotite surface area ratio such that between 80 to 20% of the Sr weathering was with a plagioclase:biotite surface area ratio found in the soil at 0 to 10 cm depth, and the remaining Sr weathering was with a plagioclase:biotite surface area ratio found in the soil at 20 to 30 cm depth. Next, we calculated the weathering end member when 60% of the Sr weathering was with a plagioclase:biotite surface area ratio found in the 0 to 10 cm surface soil, and 40% with a plagioclase:biotite surface area ratio in the soil at 20 to 30 cm depth, while varying the ratio of plagioclase:biotite Sr weathering rates between 1:1.5 and 1:10.

Ca weathering rates were calculated according to (after Wickman (1996), see derivation in the Appendix):

$$W_{Ca} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O} D_{Sr} \frac{r_{Ca}}{r_{Sr}} \qquad (2)$$

where W_{Ca} is the Ca weathering rate ($mg\,m^{-2}\,yr^{-1}$), Sr_O is the isotope ratio of the Sr lost from the soil, D_{Sr} is the Sr in atmospheric deposition ($mg\,m^{-2}\,yr^{-1}$), and

r_{Ca}/r_{Sr} is the ratio of Ca to Sr released by mineral weathering. During the life span of a tree the loss associated with Sr_O is equal to the loss through water drainage or leaching and the increment stored in living and dead biomass (see Figure 2). The ratio r_{Ca}/r_{Sr} was taken as the Ca/Sr mass ratio in the soils at 0 to 20 cm depth. Annual atmospheric deposition of Sr was estimated from the water volumes and concentrations of Ca in weekly sampled bulk deposition, the average volume-adjusted Ca/Sr ratios from the four pooled atmospheric deposition samples, and precipitation data collected at a weather station within ten kilometers of our site, in Norfolk, Connecticut. We could find no direct evidence that tree species affect Ca or Sr dry atmospheric deposition. According to Lindberg et al. (1986) most of the dry deposition in Temperate forests of the northeastern US is in particles > 2 μm in diameter and occurs under the influence of gravity. Assuming similar behavior of Ca and Sr in atmospheric deposition, we therefore believe that atmospheric Sr will not be significantly different among tree species. The isotope ratio of Sr lost from the soil (Sr_O) has been estimated as follows. Since organisms do not differentiate between the two Sr isotopes (Gosz and Moore 1989), the $^{87}Sr/^{86}Sr$ or $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio of the living and dead biomass will be indistinguishable and equal to the ratio in the stem wood. Strontium lost from the soil is the sum of leaching plus living and dead biomass storage, so Sr_O can be calculated from a relationship similar to mixing Equation (1) using the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratios of leaching Sr_L and stem wood Sr_B as the end members:

$$Sr_O = Sr_L - \frac{B_{Sr}}{O_{Sr}}(Sr_L - Sr_B) \tag{3}$$

In Equation (3) O_{Sr} is the Sr lost from the soil and B_{Sr} is the net storage of Sr in the living and dead biomass (in $mg\,m^2\,yr^{-1}$). When B_{Sr} is relatively small compared to O_{Sr} (i.e. leaching >> biomass increment) and/or when Sr_L is close to Sr_B, then Sr_O can be substituted with Sr_L (see Equation (3)). We further assumed that solutions that percolate through these coarse textured soils are well mixed at 20 cm depth and that the Sr isotopes, measured in solutions from the tension lysimeters, are in agreement with the actual Sr isotopes that leach below 20 cm. Several studies have shown that differences in solution chemistry from different types of lysimeters (Ranger et al. 1993), or solution volume from the same type of lysimeter (Cochran et al. 1970) are related to soil physical properties. A study by Shepard et al. (1990) found no significant differences in soil solution concentrations among four types of lysimeters (tension, zero tension, fritted glass, and ceramic plate) from coarse-loamy soils.

Differences in soil mineralogy between sugar maple and hemlock sites were statistically analyzed by t-tests. Linear regression models were fitted for each combination of dependent variable (Ca weathering rate and Sr in wood derived from weathering) and tree species, as a function of the Ca or Sr content (covariate) using the General Linear Model procedure in SPSS (version 7.5). Total Ca, Sr and Ca/Sr ratios in stem wood appeared to be independent of Ca, Sr and Ca/Sr ratio in the
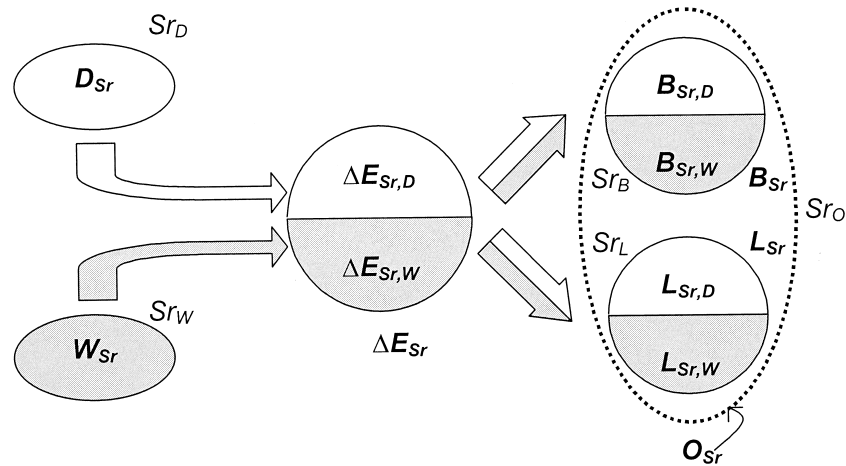
Figure 2. The flow of atmospheric (white) and weathered (gray) strontium through a forest ecosystem. D_{Sr} = atmospheric deposition, W_{Sr} = mineral weathering, ΔE_{Sr} = the net change in the exchangeable soil pool, B_{Sr} = net biomass storage, L_{Sr} = leaching, O_{Sr} = Sr lost from the soil. Sr_x = the Sr isotope ratio in flow X.

soil respectively. To test differences in total Ca, Sr and Ca/Sr ratios measured in stem wood between tree species, Post Hoc one-way ANOVA analyses (Tukey's test) were done.

Results

Soil texture was similar at all sites. All soils were high in sand and loam, and showed a small but significant decrease in clay content with depth (Table 1). Soil texture did not differ significantly under different tree species. The high organic matter contents in the first 10 cm of the soil may have been caused by contamination from the O horizon, since distinction between O and A horizon was not always clear. Besides quartz, alkali-feldspar, plagioclase and biotite were the dominant minerals in soils at the sugar maple and hemlock sites and the variation between sites and with depth was high (Table 2). At a given soil depth, the average relative surface areas (% of total mineral surface area) of plagioclase and of biotite in the 50 to 500 μm fraction and of biotite in the 10 to 50 μm fraction were invariably lower beneath hemlock than beneath sugar maple, although differences were not always significant. Biotite surface areas were markedly lower in the 0 to 10 cm soil layer compared to the 20 to 30 cm soil layer.

The Ca/Sr ratios of the soil from 0 to 20 cm depth were slightly lower than from 50 to 70 cm depth (Figure 3). The Ca/Sr ratios in stem wood were all higher than the ones measured in the soil and in the soil solution at 20 cm depth, but lower than the atmospheric deposition ratios, except for one hemlock sample. The Ca/Sr ratio in stem wood was significantly higher for hemlock than for the other tree spe-

Table 1. Average sand, silt and clay fraction and organic matter content (%) of the mineral soils at 0 to 10 cm, 20 to 30 cm, and 50 to 70 cm depth (standard error in parentheses, n = 18).

Soil property	Depth		
	0–10 cm	20–30 cm	50–70 cm
Sand (%)	42.2 (2.4)	45.2 (2.5)	46.9 (2.8)
Silt (%)	48.9 (1.8)	50.7 (1.8)	47.1 (2.2)
Clay (%)	8.9 (0.8)	7.5 (0.5)	6.1 (0.7)
Organic matter (%)	15.6 (12.0)	5.0 (2.4)	2.2 (0.7)

cies (Table 3), even though they grew in soils with a similar Ca/Sr ratio. All species displayed large but comparable variability in wood Ca concentration, but stem wood of hemlock was significantly lower in Sr concentration than that of other species (Table 3).

The $^{87}Sr/^{86}Sr$ ratios measured in atmospheric deposition showed no significant temporal variation (Table 4), with a weighted average of 0.71021. The $^{87}Sr/^{86}Sr$ ratio in the stem wood and soil water samples among sites varied more, while the $^{87}Sr/^{86}Sr$ ratio in soil water was generally comparable to the ratio of the stem wood sample measured at the same site (difference < 0.2%). Although differing in age between 40 and 130 years, the stem wood samples of six individual beech trees at one site showed very little variation in the $^{87}Sr/^{86}Sr$ ratio (Table 4). The variation in $^{87}Sr/^{86}Sr$ ratio among the bulk soil samples at 50 to 70 cm depth varied less than the individual minerals (Table 4).

The proportion of the Sr in the wood derived from weathering was calculated for each site according to Equation (1). We used the $^{87}Sr/^{86}Sr$ ratio measured in the bulk soil at 50 to 70 cm depth at each site as the weathering end member for that site. Between 39 and 63% of the Sr in the biomass of all tree species was derived from soil weathering (Figure 4). With three replicates per tree species no significant differences in the weathering derived Sr were observed among tree species. However, there was a significant positive correlation with the Sr content in the soil (P < 0.005). The Ca weathering rate in the rooting zone at each site was estimated by Equation (2), again using the $^{87}Sr/^{86}Sr$ ratio measured in the bulk soil at 50 to 70 cm depth at each site as the weathering end member for that site. Strontium atmospheric deposition was 0.42 mg m^{-2} yr^{-1} (compared to 180 mg m^{-2} yr^{-1} for Ca with concentrations ranging between 45 and 250 μg L^{-1}). We used the Ca/Sr ratio measured in the first 20 cm of the soil as the proportional release of Ca and Sr through weathering (r_{Ca}/r_{Sr}) and the the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio in the soil water sampled from the lysimeters at 20 cm depth (Sr_L) as the ratio of Sr lost from the soil (Sr_O). As with Sr, we did not observe significant differences in the Ca weathering rate in the surface soil among tree species (Figure 5). Rather, the Ca weathering rate significantly increased with total amount of Ca in these soils (P < 0.001).

The sensitivity of the Ca weathering rate (as calculated from Equation (2)) to variations in the composition of the weathering end member was evaluated for the sugar maple and hemlock sites (Figure 6). For the two scenarios (plagioclase-bi-

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Table 2. The average proportion of alkali-feldspar, plagioclase and biotite (% of total mineral surface area) in the 50 to 500 μm fraction and of biotite in the 10 to 50 μm fraction of mineral soils at 0 to 10 cm, 20 to 30 cm, and 50 to 70 cm depth beneath sugar maple and hemlock sites (standard error in parentheses, n = 3). Significant differences between tree species are indicated as ns: not significant, *: P < 0.1, and **: P < 0.01 (t-test).

| Soil depth (cm)	Alkali-feldspar (%) 50–500 μm		Plagioclase (%) 50–500 μm		Biotite (%) 50–500 μm		Biotite 10–50 μm	
(cm)	Acer saccharum	Tsuga canadensis	Acer saccharum	Tsuga canadensis	Acer saccharum	Tsuga canadensis	Acer saccharum	Tsuga canadensis
0–10	13.8 (5.3)	13.7 (5.1) ns	15.7 (2.7)	6.9 (1.8) *	6.5 (4.2)	1.3 (0.4) ns	9.1 (3.6)	0.5 (0.2) *
20–30	6.2 (0.4)	13.4 (1.6) *	11.5 (1.6)	3.0 (0.8) **	23.2 (8.7)	3.8 (0.7) *	13.0 (2.1)	7.6 (2.8) ns
50–70	11.4 (1.3)	12.0 (1.8) ns	6.8 (1.3)	4.7 (0.6) ns	12.7 (4.3)	4.7 (0.9) ns	25.6 (4.2)	13.8 (2.4) *
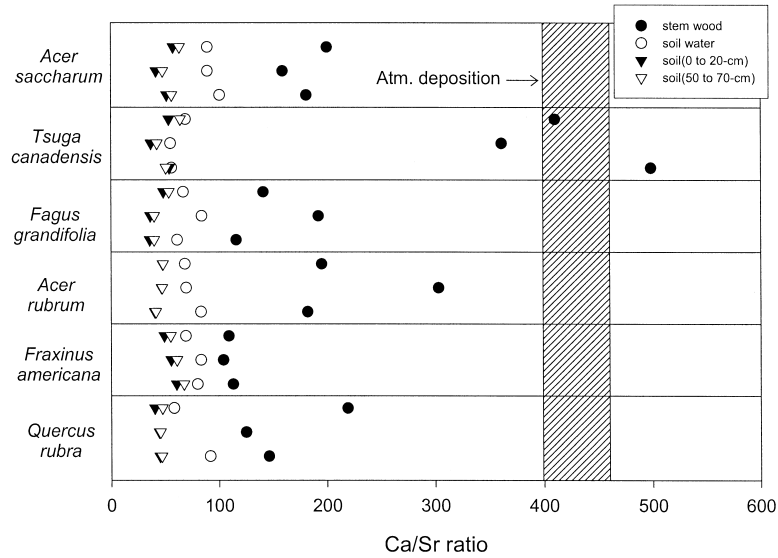
Figure 3. The Ca/Sr ratio in atmospheric deposition, in the soil (0 to 20 cm and 50 to 70 cm depth), soil water and stem wood for each site dominated by one of the six tree species.

Table 3. Average total Ca and Sr content and Ca/Sr ratios measured in stem wood for different tree species (standard error in parentheses, n = 3).

Tree species	Ca ($\mu g\,g^{-1}$)	Sr ($\mu g\,g^{-1}$)	Ca/Sr
Acer saccharum	990 (136) a[1]	5.53 (0.61) a	180 (11.8) a
Tsuga canadensis	943 (73) a	2.25 (0.13) b	423 (40.1) b
Fagus grandifolia	867 (243) a	5.61 (0.61) a	150 (22.3) a
Acer rubrum	1041 (129) a	4.68 (0.33) a	227 (38.3) a
Fraxinus americanum	741 (145) a	6.93 (0.87) a	107 (12.8) a
Quercus rubra	1047 (137) a	5.71 (0.96) a	183 (30.0) a

[1] different letters indicate significant differences between tree-species (P < 0.05) with one-way ANOVA, Post Hoc Tukey test.

otite composition effect, Figure 6A, and plagioclase:biotite weathering effect, Figure 6B), the rate of Ca weathering increased on average with the total Ca content in the soil. Dotted lines in Figure 6 show the regression of the average value of Ca weathering at each site with the total Ca concentration in the soil. At all sites the Ca weathering rate decreased as more weathering took place with mineral ratios found at greater depth, and as weathering rates of biotite increased relative to those of plagioclase. The maximum values of Ca weathering that were calculated for sugar maple sites were higher than for hemlock, but not significantly so (P = 0.11 for plagioclase-biotite composition effect and P = 0.13 for weathering rate effect). The minimum values of Ca weathering showed a positive relation with the total Ca concentration in the first 20 cm of the mineral soil (P = 0.10 for plagioclase:biotite
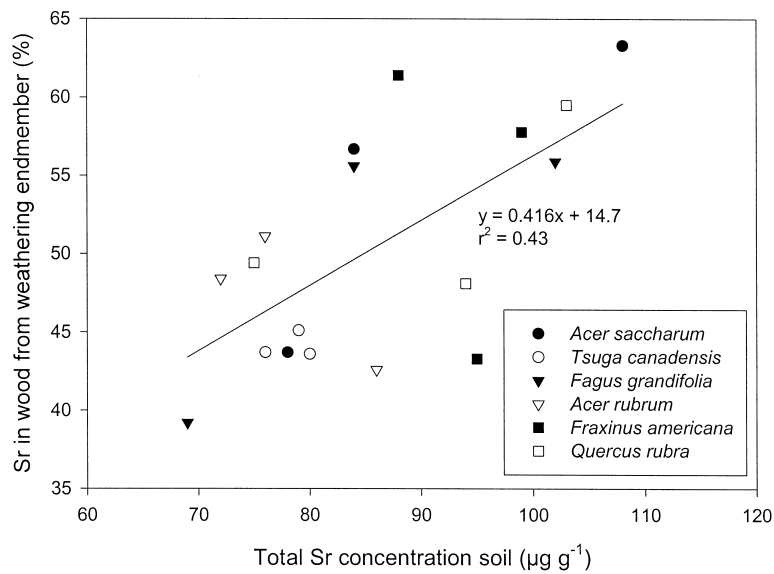
Figure 4. The proportion of Sr in stem wood derived from soil weathering (% of total Sr in wood) as a function of the total Sr concentration in the first 20 cm of the soil for the different tree-species.
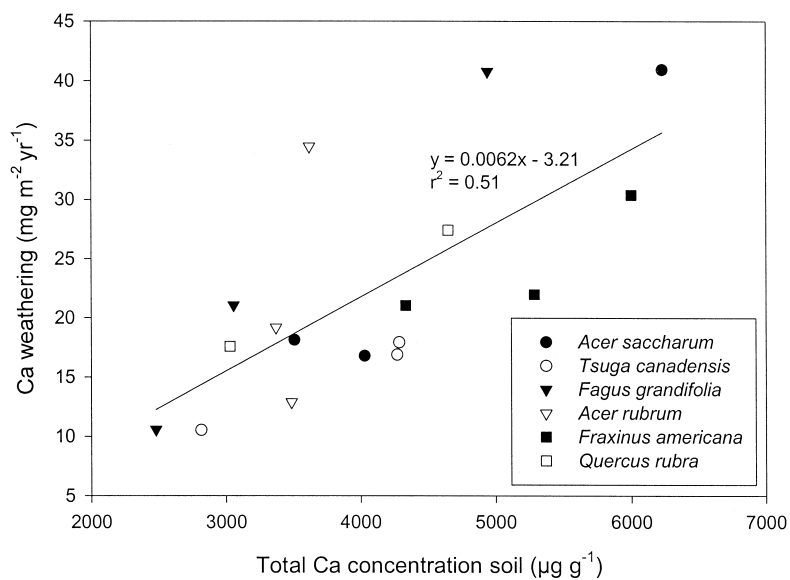

Figure 5. The Ca weathering rate in the first 20 cm of the soil as a function of the total Ca concentration in the first 20 cm of the soil for the different tree species.

composition effect and P = 0.05 for weathering rate effect), but no tree species effect.

A. Plagioclase-biotite composition effect

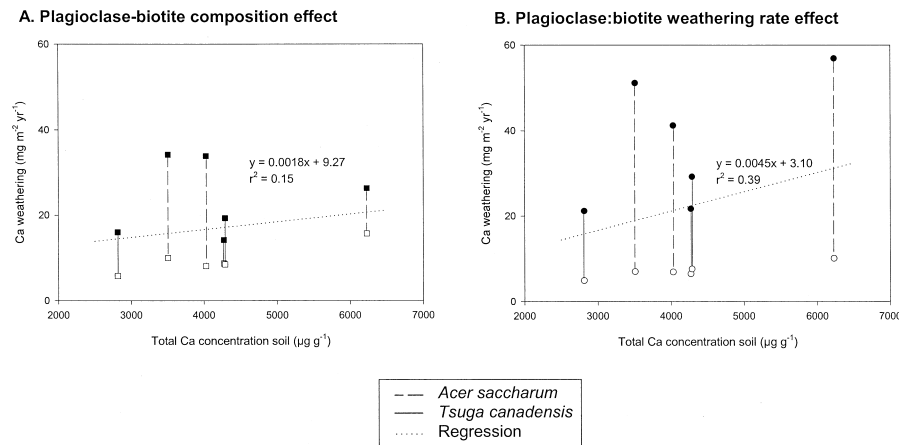**B. Plagioclase:biotite weathering rate effect**

Figure 6. The relationship between Ca weathering rate and total soil Ca concentration in the first 20 cm of the soil for sugar maple and hemlock sites, calculated by different assumptions about the weathering end member. A. Effects of variations in weathering end member due to different plagioclase-biotite surface area ratios. B. Effects of different ratios of the plagioclase:biotite weathering rates. Vertical lines show the variation on Ca weathering under sugar maple (dashed line) and hemlock (solid line). Open squares: 20% of Sr weathering takes place at 0 to 10 cm depth, and 80% at 20 to 30 cm depth; filled squares: 80% of Sr weathering takes place at 0 to 10 cm depth and 20% at 20 to 30 cm depth. Open circles: plagioclase:biotite weathering rate = 1:10; filled circles: plagioclase:biotite weathering rate = 1:1.5. Dotted lines are the regressions of the average Ca weathering rate at each site with total Ca concentration in the soil. See text for details.

Discussion

The heterogeneity of the soil mineral composition between sites and with depth, a common feature of soils formed from glacial deposits, hampered the interpretation of our results. Lower relative surface areas of plagioclase and biotite in the surface soil beneath hemlock than beneath sugar maple suggest more intense soil weathering beneath hemlock. The low number of replicates prevented us from detecting very strong patterns, but allowed us to undertake a sensitivity analysis on the Ca weathering calculations, which was our main goal from these results.

The higher Ca/Sr ratio in stem wood than in soil solution at 20 cm depth beneath all tree species could mean that most of the Ca and Sr is taken up above a depth of 20 cm in soil, where the Ca/Sr ratio in soil solution is probably higher and closer to the Ca/Sr ratio in atmospheric deposition. The Ca/Sr ratio in stem wood of hemlock, was highest and close to the Ca/Sr ratio in atmospheric deposition. This finding suggests that hemlock utilizes much atmospheric Ca and Sr. Indeed, root length measurements at these sites showed that hemlock had significantly more of its total fine root length in the forest floor and upper 30 cm of the mineral soil than sugar maple (Dijkstra and Smits, submitted). On the other hand, Poszwa et al. (2000) found that spruce (*Picea abies*) preferentially took up Ca over Sr on acid

soils in a forest in France. Preferential uptake of Ca over Sr could also explain the relatively high Ca/Sr ratio in stem wood of hemlock.

The weighted average $^{87}Sr/^{86}Sr$ ratio we calculated for the atmospheric end member (0.71021) was slightly higher than the present-day ratio of sea water (0.709198, Hess et al. (1986). Our $^{87}Sr/^{86}Sr$ ratios in atmospheric deposition were very similar to those found by others in the northeastern US (Bailey et al. 1996; Dasch 1969; Miller et al. 1993). In addition, those earlier studies also showed that the $^{87}Sr/^{86}Sr$ ratio in atmospheric deposition is relatively constant over time. We are therefore confident that the weighted average $^{87}Sr/^{86}Sr$ ratio of 0.71021 is a good approximation of the atmospheric end member.

Similarity between $^{87}Sr/^{86}Sr$ ratios in stem wood samples and in soil solutions implies that the turnover of Sr within the ecosystem was rapid compared to the rate of its addition from either weathering or atmospheric input (Graustein 1989). The small variation in the $^{87}Sr/^{86}Sr$ ratio of stem wood from closely spaced beech trees, of different age at one of our sites, suggests that there is no significant change in the pool of weathered Sr during the single lifetime of the trees. By contrast, Åberg (1995) concluded that a temporal change in the pool of weathered Sr in the soil was responsible for the variability in the $^{87}Sr/^{86}Sr$ ratio found in different tree rings.

Given the low organic matter content (2.2%) at 50 to 70 cm depth, variation of the $^{87}Sr/^{86}Sr$ ratio in the bulk soil at 50 to 70 cm depth must have been caused by variations in soil mineral concentration. Minerals such as biotite, muscovite (micas) and vermiculite (weathering product of biotite) had much higher $^{87}Sr/^{86}Sr$ ratios than plagioclase.

In assessing the proportion of Sr in stem wood derived from weathering according to Equation (1) and the Ca weathering rate according to Equation (2), we approached the problem of identifying a weathering end member in two ways. First, in view of the relatively large variation in the Sr isotope composition of the soils, we used the isotope ratio of total Sr in the soil at 50 to 70 cm depth at each site as the site-specific ratio for the weathering end member. Second, because of the large variability in mineralogy with soil depth and likely differences in relative weathering rates among feldspars and biotite, we tested the sensitivity of the calculated weathering rates to the choice of a site-specific weathering end member (see below).

Based on the isotope ratio of total Sr in the soil at 50 to 70 cm depth, between 39 and 63% of the Sr in stem wood of all tree species is derived from soil weathering. Other studies at sites with similar soils gave similar values, between 47 (Miller et al. 1993) and 68% (Bailey et al. 1996). On soils in Hawaii of different age, between 20 and 90% of wood Sr was attributed to weathering (Chadwick et al. 1999).

Our Ca weathering rates (between 11 and 41 mg m^{-2} yr^{-1}) are low compared to those from other studies in the same region. Bailey et al. (1996) estimated a Ca weathering rate of 120 mg m^{-2} yr^{-1} for the Cone Pond Watershed in New Hampshire. The most recent estimate of Ca weathering at the Hubbard Brook Experimental Forest is 228–312 mg m^{-2} yr^{-1} (Likens et al. 1998). Lower Ca weathering at our site could be due to different composition and abundance of weatherable

minerals in our soils and because our soils are shallower than those at the sites in New Hampshire (S.W. Bailey, personal communication). Further, estimates by Bailey et al. (1996) and Likens et al. (1998) are based on whole watersheds where weathering from deeper unconsolidated material may have contributed to their higher numbers. At current weathering rates, the upper 20 cm of the mineral soil at our sites would be depleted of Ca in 26,000 to 32,000 years.

Our Ca weathering rates calculations are based on the assumption that the isotope ratio of Sr lost from the soil (Sr_O) can be substituted with the isotope ratio of Sr lost by leaching at 20 cm (Sr_L). As outlined in the method section, this is only justified when i) the net biomass storage of Sr (B_{Sr}) is small compared to Sr leaching and/or ii) when Sr_L is close to the Sr isotope ratio of stem wood (Sr_B). The Sr_L values that we measured were sometimes higher, and sometimes lower than the Sr_B values (Table 4), but were always fairly close to each other at each site, so that the second criteria was partly met. We have no data on net biomass storage of Sr at our sites. Net Ca uptake in above and below ground biomass was around 25% of the Ca loss through leaching at the Hubbard Brook Experimental Forest in New Hampshire (Likens et al. 1998). When at our sites 25% of the annual Sr loss in the system goes into biomass storage, then our Ca weathering rates calculations would have an error ranging between −14 and +16%.

Both the proportion of Sr in stem wood derived from soil weathering and the Ca weathering rate showed significant positive trends with total Sr and Ca concentration in the soil respectively. The highly significant correlation between total Ca concentration in the first 20 cm of the mineral soil and the plagioclase surface area measured in the first 10 cm of the mineral soil ($r^2 = 0.70$, $P < 0.001$) suggests that plagioclase is the most important source of Ca weathering in these soils.

Varying the weathering end member based on the measured variability in biotite and plagioclase contents at sugar maple and hemlock sites, and considering different relative weathering rates of these two minerals, we found a relatively large range of Ca weathering rates at each site. However, the maximum calculated Ca weathering rate, 60 mg m^{-2} yr^{-1}, was, relative to other studies, still low. The fact that plagioclase and biotite were quantitatively important weatherable minerals with distinctly different $^{87}Sr/^{86}Sr$ ratios (Table 4), increased the sensitivity of our analysis. The Sr isotope method we used to determine the species effects on weathering rates is not sensitive enough to detect significant differences.

Direct mineralogical observations, on the other hand, suggest that under hemlock, biotite may have undergone stronger weathering than under sugar maple. Especially in the first 10 cm of the mineral soil we found indication of more intense weathering beneath hemlock. Biotite mineral staining by iron oxide (biotite grains with darker color), as a result of weathering, was more pronounced in the upper 10 cm of the soil beneath hemlock than beneath sugar maple. Optical observations in a 7 × 7 -cm thin section from an undisturbed soil sample beneath hemlock showed complete absence of biotite in the first 3 cm of the mineral soil, and also plagioclase showed more frayed surfaces in the upper centimeters (F.A. Dijkstra, unpublished). Biotite appeared to have higher weathering rates than alkali-feldspar and plagioclase in the upper 10 cm of the soil and may have weathered faster beneath

Table 4. Strontium isotope ratios and Sr concentrations in atmospheric deposition and soil minerals, and $^{87}Sr/^{86}Sr$ ratios in bulk mineral soil from 50 to 70 cm depth, soil solution from 20 cm depth and stem wood for each site dominated by one of the tree species.

	$^{87}Sr/^{86}Sr$	$Sr\ (\mu g\ L^{-1})$	
Atmospheric deposition			
15 May–12 Jun 1998	0.70999	0.61	
19Jun–23 Jul 1998	0.71000	0.28	
21 Aug–19 Sep 1998	0.71073	0.61	
29 Sep–17 Oct 1998	0.71033	0.11	
Soil minerals	$^{87}Sr/^{86}Sr$	$Sr\ (\mu g\ g^{-1})$	
Quartz	0.72498	1.7	
Alkali-feldspar	0.72999	206.5	
Plagioclase	0.71117	379.4	
Biotite	0.75496	63.8	
Muscovite	0.76438	44.3	
Vermiculite	0.75141	33.7	
Site-species	Soil	Soil solution $^{87}Sr/^{86}Sr$	Wood
Acer	0.72680	0.71745	0.71742
saccharum	0.72746	0.71898	0.71995
	0.72564	0.71991	0.71957
Tsuga	0.72816	0.71786	0.71827
canadensis	0.72969	0.71807	0.71867
	0.72963	0.71881	0.71862
Fagus	0.72442	0.71607	0.71574
grandifolia	0.72399	0.71940	0.71789
	0.72150	0.71675	0.71627
			0.71634
			0.71637
			0.71640
			0.71647
			0.71651
Acer	0.72577	0.71691	0.71680
rubrum	0.72491	0.71747	0.71730
	0.72726	0.72100	0.71889
Fraxinus	0.72442	0.71795	0.71840
americana	0.72520	0.71748	0.71667
	0.72069	0.71550	0.71662
Quercus	0.72453	0.71867	0.71870
rubra	0.72713	0.71882	0.71853
	0.72645		0.71797

the ectomycorrhizal hemlock than beneath the endomycorrhizal sugar maple. Wal-

lander (2000) showed that tree species associated with ectomycorrhiza stimulated K uptake and biotite weathering.

If hemlock stimulates biotite over plagioclase weathering more than sugar maple, then the weathering end member would be at the higher end and the Ca weathering rate at the lower end of our estimates at hemlock sites. This result contradicts our hypothesis that the acidifying hemlock increases Ca weathering in the surface soil. Because of overall slow soil weathering, the stronger weathered character of especially biotite below hemlock may have been the result of more intense biotite weathering over a period of several generations of hemlock trees.

Conclusions

Optical mineral analysis suggests that biotite weathering in the upper 10 cm of the soil is more intense beneath hemlock than beneath sugar maple. However, with the Sr isotope study, we were unable to detect significant differences in Ca weathering beneath the six tree species studied here, regardless of a range of assumptions about the weathering end member. The inferred rate of Ca weathering was low (< 60 $mg\,m^{-2}\,yr^{-1}$) in these acidic soils, and positively related to the total Ca concentration in the surface soil (presumably mainly from plagioclase).

Organic acid production and increased soil acidity are mechanisms suggested to influence soil weathering. Higher amounts of dissolved organic acids in the soil solution beneath hemlock (Dijkstra et al. 2001) may have caused higher weathering intensities in the upper mineral soil. However, the annual supply of Ca for plant uptake through soil weathering in these acidic soils derived from granitic material, appears to be very low for all tree species. The role of soil organic acids in mineral weathering processes is still controversial. Other studies have also suggested that organic acids have no large effect on the dissolution rates of primary Ca minerals of granitic rocks, but may be more effective on more mafic rock types (Drever and Vance 1994; Raulund-Rasmussen et al. 1998). Within the sensitivity of our method, this research indicates that the tree species studied here do not have a significant distinct effect on the Ca and Sr weathering rates in acidic surface soils.

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Appendix

Derivation of weathering equation

The fraction of the atmospheric Sr in a Sr mixture of both atmospheric and weathering sources ($X_{mix,D}$) is given by (after Graustein (1989)):

$$X_{mix,D} = \frac{Sr_W - Sr_{mix}}{Sr_W - Sr_D} \tag{4}$$

where Sr_W is the Sr isotope ratio $^{87}Sr/[^{87}Sr + ^{86}Sr]$ of the weathering end member, Sr_{mix} is the isotope ratio of the mixture and Sr_D is the isotope ratio of the atmospheric end member. A simple Sr budget for a tree site during a tree's life span is given by (see also Figure 2):

$$\Delta E_{Sr} = D_{Sr} + W_{Sr} - O_{Sr} \tag{5}$$

where ΔE_{Sr} is the net change in the exchangeable pool in the soil, D_{Sr} is the atmospheric deposition of Sr, W_{Sr} is the mineral weathering of Sr and O_{Sr} is the total loss of Sr from the soil (i.e., leaching below the rooting zone L_{Sr} and net biomass increment and fixation of Sr in litter B_{Sr}). All fluxes are given in mg m^{-2} yr^{-1}. The change in atmospheric Sr in the exchangeable pool in the soil $\Delta E_{Sr,D}$ can be written as:

$$\Delta E_{Sr,D} = D_{Sr} - O_{Sr,D} \tag{6}$$

where $O_{Sr,D}$ is the flux of atmospheric Sr lost from the soil. With:

$$O_{Sr,D} = X_{O,D}O_{Sr} \tag{7}$$

(Equation 6) can be written as:

$$\Delta E_{Sr,D} = D_{Sr} - X_{O,D}O_{Sr} \tag{8}$$

where $X_{O,D}$ is the fraction of atmospheric Sr lost from the soil. The total net change of Sr in the exchangeable pool can be written as:

$$\Delta E_{Sr} = \Delta E_{Sr,D} + \Delta E_{Sr,W} \tag{9}$$

where $\Delta E_{Sr,W}$ is the change in the amount of weathered Sr in the exchangeable pool

in the soil. The fraction of atmospheric Sr in the net change of Sr in the exchangeable pool will be equal to the fraction of atmospheric Sr lost from the soil:

$$\frac{\Delta E_{Sr,D}}{\Delta E_{Sr,D} + \Delta E_{Sr,W}} = X_{O,D} \tag{10}$$

Substituting $\Delta E_{Sr,D}$ of Equation 8 into Equation 10, $\Delta E_{Sr,W}$ can be expressed as:

$$\Delta E_{Sr,W} = \frac{(1 - X_{O,D})(D_{Sr} - X_{O,D}O_{Sr})}{X_{O,D}} \tag{11}$$

Similar to Equation 6 the change in the weathered Sr in the exchangeable pool can also be written as:

$$\Delta E_{Sr,W} = W_{Sr} - (1 - X_{O,D})O_{Sr} \tag{12}$$

Using Equation 11 and 12, eliminating the terms $\Delta E_{Sr,W}$ and O_{Sr}, the mineral weathering of Sr can be expressed as:

$$W_{Sr} = \frac{(1 - X_{O,D})D_{Sr}}{X_{O,D}} \tag{13}$$

and with Equation 4:

$$W_{Sr} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O}D_{Sr} \tag{14}$$

where Sr_O is the isotope ratio of the Sr lost from the soil. The Ca weathering rate W_{Ca} can be calculated by multiplying the Sr weathering rate with the Ca to Sr weathering ratio r_{Ca}/r_{Sr}:

$$W_{Ca} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O}D_{Sr}\frac{r_{Ca}}{r_{Sr}} \tag{15}$$

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